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Concern for Acidic Deposition in the Great Lakes Region

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16. ABSTRACT

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ACID PRECIPITATION

Effects on Ecological Systems

Edited by
FRANK M. D'ITRI

ANN ARBOR SCIENCE
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CHAPTER 2

THE CONCERN FOR ACIDIC DEPOSITION IN THE GREAT LAKES REGION

Orie L. Loucks
The Institute of Ecology
Indianapolis, Indiana

INTRODUCTION

The Great Lakes region of the United States and Canada is an especially appropriate focus for a conference on acid rain in 1981 for one paramount reason: If the evidence is compelling that environmental alterations from acidic deposition could, indeed, be of the type and magnitude being alleged in other regions, then there are urgent decisions and actions needed now to prevent those effects from being expressed here. A principal conference goal, therefore, must be to review the evidence as it applies to the unaltered, or slightly altered, Great Lakes region, and to consider what new data or relationships still need documentation before mitigation or control strategies can be evaluated. My goal will be to outline why a lightly impacted region can be so important to the perspectives of both Canada and the United States, and to highlight the implications of certain recent insights on effects processes which may not be covered in later chapters.

IS ACIDIC DEPOSITION A PROBLEM?

One must ask, first, whether acidification of rainfall is really a problem, and, in particular, what criteria one should use to judge whether it is serious in the national or international perspective. Although questions remain about details of the atmospheric chemistry, acidic substances are known to be produced in the atmosphere when sulfur dioxide (SO_2) and nitrogen oxides (NO_x) from fossil fuel combustion combine with oxygen to produce sulfuric and nitric acids. We also know now that under appropriate weather conditions these pollutants can be carried hundreds of kilometers from their source. Some

of the acid-forming emissions can be taken up by vegetation as gases, and, following sulfate formation, others drop out as particles in processes called dry deposition. Only about half of the products from acid-forming precursors are washed from the air by rain, snow, or mist, yielding acid rain. The remainder enter into dry deposition or are carried off the continent.

But, many people ask, "What could be the source of the acidic deposition on a remote Wisconsin lake and who is culpable?" Consider the pattern of gaseous emissions from the industrial heartland and the cities of the Great Lakes region. Pollutant concentrations frequently build up and then move long distances over the rural landscape. Many questions remain as to the distance transported and ultimate effects, but techniques of source/receptor matrix analysis, and of air parcel trajectory analysis, are beginning to tell us much about the patterns of pollutant transport over periods of 12 to 24 hr before emerging as dry or wet deposition over an area such as the Great Lakes Basin.

A series of recent reviews (e.g., Last et al., 1980; Overrein, 1980) has shown that, despite some questions of rates of reactions and of control mechanisms, we know enough about the acidic deposition phenomenon now to describe the general transport and formation of acid, the areas of impact, the mechanisms of effect, and the basis for some lags in watershed response times. One can conclude now that there is a problem being expressed in the alteration of resources over time, and that it is strongly linked to acid-forming industrial and residential emissions. A principal question for the research agenda at this meeting, therefore, is whether this is a problem in the western Great Lakes states. Figure 1 shows the flow relationships among the principal ecological consequences believed to result from fossil fuel emissions and the subsequent deposition of increased hydrogen, sulfate, and nitrate on the landscape. The apparent effects from this deposition must be examined as responses to chemical alteration of a coupled system which, for simplicity, is shown here as a flow diagram.

THE REGION OF CONCERN

The resource systems of concern to a conference in the Great Lakes region are principally those of the northern tier of states from Minnesota to New York, the northern half of states bordering the Ohio River, and the Province of Ontario. The region is potentially susceptible to acid deposition (Galloway and Cowling, 1978) because its coarse-textured soils

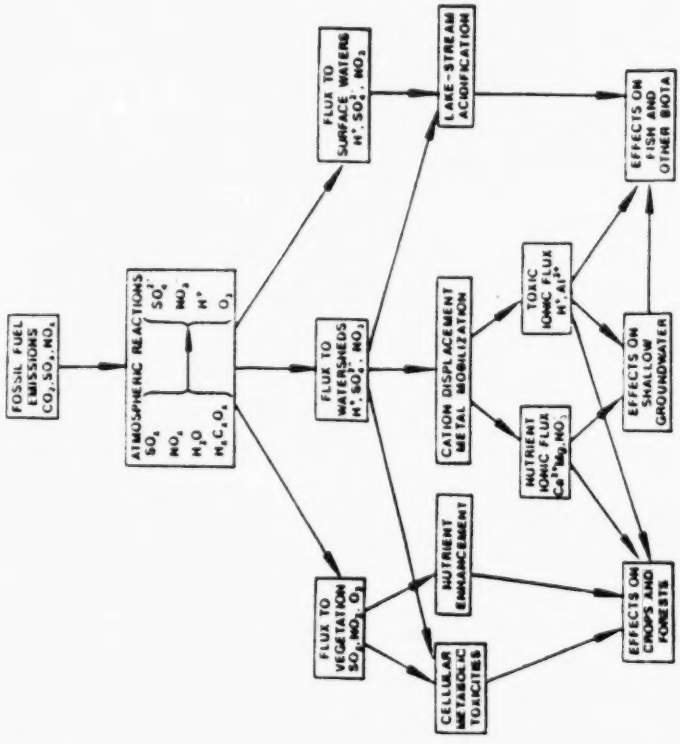

Figure 1. Flow diagram showing system linkages from acid and ozone-forming precursors through atmospheric acid formation, deposition, and, finally, effects.

are very low in calcium carbonate and are underlain by chemically inert igneous and metamorphic bedrocks and poorly buffered sandstone. The region's rich resources and industries, including recreation, forestry, farming, and mining, could be vulnerable to disruption if acid inputs reached levels presently being experienced in areas of Europe and the northern Appalachian region of the United States.

The advance of ice masses over these states during the pleistocene era scoured weathered bedrock from the higher land areas and deposited the earth and rock far to the south. What remained was only the coarsest fraction of the soil which, together with boulders and local deposits of outwash sand, makes up most of the surface deposits in the northern half of the western Great Lakes states and in much of Ontario.

Glacial activity throughout the region left thousands of depressions in the landscape, yielding an unusual abundance of lakes and waterways. These are now in high demand for recreation and fishing and are the basis for the local economy in many parts of the Great Lakes region. Here, clean water is essential, both for game fish species and human uses. Because of the outstanding quality of the aquatic resources, recreation dominates the economy locally and over relatively large areas, with large parts of the population supported to some degree by water-related industries.

Water resource inventories in this region indicate that Minnesota has a minimum of 15,000 lakes, and up to 22,000, if smaller lakes (to 2.03 ha) are counted. These lakes cover 10,360 km^2, or one-twentieth of the land area of the state. Wisconsin has some 11,000 lakes over 4.1 ha in size, mostly in the northern half of the state. Wisconsin also has 2,250 trout streams, totalling 13,982 ha of trout water. The upper peninsula of Michigan has a very large number of low alkalinity lakes likely to be sensitive to acid inputs (Schneider, 1975). Of some 8,000 lakes and ponds in the western half of the upper peninsula alone, more than 50 percent have an alkalinity in the range of 10 mg/l, indicating they are potentially susceptible to acid inputs. Ontario has estimated its lake inventory at 180,000 or more (MOE, 1980), reflecting an area some three times larger than the lake districts of the western Great Lakes states.

These states, Ontario, and the United States federal government have all tried to meet public demand for access to aquatic resources by establishing a large number of state forests, parks, and wild rivers, each of which represents a large public investment for the benefit of posterity. The state

of Wisconsin estimated the use of state-owned parks and forests at more than 11 million visitors per year between 1971 and 1973 (the most recent statistic available). More than 10 million tourists each year visit the state of Michigan. The loss of even a small number of the lakes or streams in these states could adversely affect individual services, thereby influencing the industry to some degree; how much is a matter of considerable concern to each of the governments and publics involved.

The northern regions of these states and the province of Ontario also are rich in timber, a resource that also may be affected adversely by long-term nutrient losses and metal toxicities from acid deposition. The forests of Michigan cover 8.1 million hectares, or more than one-half of the state; half of the state of Wisconsin also is covered by commercial forest. Forest growth rates are relatively good throughout the region due to a combination of warmer summer temperatures and comparatively abundant moisture supplies. However, timber production depends on the nutrient status of the soil, and there is currently no general soil-maintenance or fertilizer application program for forest soils in this region.

The resources that are most likely to be affected by acid deposition, such as recreation, forests, agriculture, and mining, are largely the responsibility of state and provincial governments. Only in air quality, and to a moderate extent in interstate water management, has the federal government been given a substantial degree of authority to assure resource protection. On the other hand, the administrative agencies of state government acting alone cannot protect the renewable resources of that state or province from the prospective long-term effects of acid deposition. Thus, it may no longer be possible for state or provincial governments to meet the historic expectation that they will protect resources and related industries in their states. At the same time, decision-making institutions in adjacent states have no compelling reason to be concerned for neighboring states. The federal government has a responsibility only to set uniform standards acceptable to all parts of the country, including highly industrialized sectors such as the Ohio Valley, and more sensitive regions such as the Great Lakes states.

Thus, a further responsiblity for these proceedings, focused on the Great Lakes region, is to examine new approaches to regional air and water quality protection that may be necessary to deal with the long-term effects of acid rain. Because of the complexity of the source/receptor system, and the cause-and-effect relationships, a very substantial scientific base will be needed before region-wide government

regulation or economic adjustments can be justified. Given the possible magnitude of the long-term pollutant deposition problem, however, it is urgent to develop studies that analyze the prospective impacts in some detail before more serious effects take place. It is for this reason, more than any other, that the potential impacts of moderate levels of acid deposition in the western Great Lakes must be considered so carefully.

ALTERATION OF ATMOSPHERIC CHEMISTRY

Precipitation chemistry is influenced by the patterns of chemicals released to the atmosphere, as well as by the large-scale atmospheric circulation as air masses move like large eddies over North America. All precipitation contains a wide variety of chemical constituents from sources such as sea spray, dust particles, and the natural cycling of carbon, nitrogen, and sulfur. Discharging wastes to the atmosphere increases the amounts of compounds containing elements such as nitrogen, carbon, and sulfur, and adds to the variety of compounds such as PCBs and heavy metals which are found in rainfall. The four ions of most importance to acid rain are: hydrogen (H^+), ammonium (NH_4^+), nitrate (NO_3^-), and sulfate (SO_4^{2-}).

The seasonal quantity and quality of precipitation also are important for determining the potential for acidic inputs to impact the environment. Acid pollutants accumulating in the snowpack have a higher potential for causing deleterious effects on organisms and habitats in areas with high snowfall than in areas with lower amounts of snow accumulation. This effect is due to the rapid flushing of accumulated acid during snowmelt. Thus, the distribution of precipitation during the year, the temporal behavior of rainfall, and the location of pollution sources within rainfall pathways are linked to the potential for damage to aquatic ecosystems. Here again, the gradient from moderate rainfall in the western Great Lakes region to higher rainfall in the East is an important consideration.

Distilled water in equilibrium with atmospheric carbon dioxide has a pH value of about 5.6. The presence of base substances such as dust can raise the pH of rainfall, and acidic substances can decrease it. Partial results on the present levels of chemical alteration of precipitation are presented in Figure 2, showing large areas of North America which received acidic precipitation in 1979. (Also see the paper by Barrie, Chapter 7, in this volume). The pH gradient from western Minnesota to New York is almost a classic gradient-type experimental manipulation.

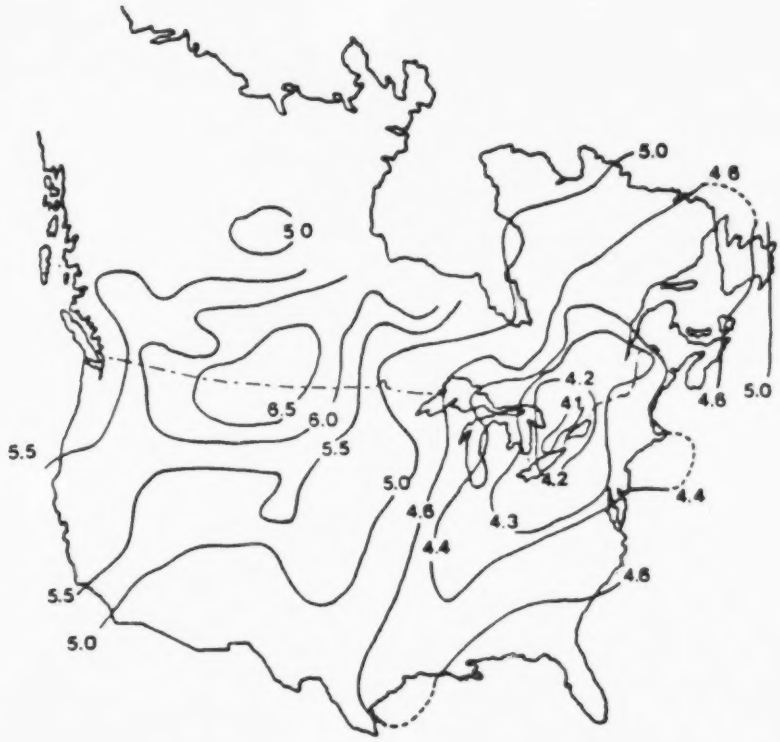

Figure 2. Isopleths of pH showing precipitation-weighted averages for April, 1979, to March, 1980. NADP and CANSAP monitoring data. (Adapted from Glass and Brydges, 1981, and Barrie, Chapter 7 of this volume.)

One often asks what the historic, pre-industrialization levels of precipitation chemistry and atmospheric deposition might have been. In 1979, a study conducted at the Boundary Waters Canoe Area (BWCA) of Minnesota and the Quetico Provincial Park in Ontario addressed this question (Glass and Loucks, 1980). The Atikokan generating station was being planned 80 to 120 km north of the BWCA. This area, until recently, has

had especially clean air. The sulfur dioxide levels at a recording site near Fernberg, Minnesota, during 1977 never exceeded the threshold level of the instrument (10 $\mu g/m^3$) and exceeded this level only once during 1978. The suspended particulate matter, as measured by a high-volume sampler, yielded an annual arithmetic average of 15 $\mu g/m^3$, and an annual geometric average of 11 $\mu g/m^3$ (Glass and Loucks, 1980).

To evaluate historic vs. modern sources of acidity, we used measurements of bulk deposition of sulfate (wet-plus-dry fall) obtained at three locations in the extreme western end of the Great Lakes region. The longest record, at the Experimental Lakes Area (ELA) in Ontario, 180 km northwest of Atikokan, shows an average recent sulfate deposition of 10.9 kg/ha/yr. The average pH of the rainfall there during the period between 1974 and 1977 was 4.86. The pre-settlement pH for rainfall in this area appears to have been 5.7 (cf. carbonic acid equilibrium, and data for 1955 to 1956 shown by Galloway and Cowling, 1978). Data from the ELA show that 70 percent of the nitrate and sulfate in the current rainfall is balanced by cations other than hydrogen. Thirty percent is in the acid form, and the H^+ ions were assumed to divide between SO_4^{2-} and NO_3^- on a 2:1 ratio. This information yields an estimate of 7.6 kg/ha/yr of sulfate balanced by Ca^{2+}, Mg^{2+}, and NH_4^+, while 3.1 kg/ha/yr is acid sulfate, producing the net depressions in pH. Thus, depending on the historic potential of atmospheric constituents other than H^+ to balance anthropogenic acid precursors, pre-settlement loadings of sulfate must lie between 0 and 7.6 kg/ha/yr. For the purposes of the BWCA studies an intermediate value of 4 kg/ha/yr was used.

POTENTIAL ALTERATION OF THE TERRESTRIAL SYSTEM

Ozone is a pollutant often involved in long-distance transport similar to that of acid rain. Elevated levels often lead to injury, and crop yield reductions have been well documented on many crop species in the Great Lakes region. These crops include tobacco, soybeans, corn, grapes, cucumber, squash, and radish. Direct effects of acid precipitation on plants are much less than those of ozone, but effects of acid rain are known on crops for which the foliage is valued. The potential impacts include:

1. damage to protective surface structures such as cuticles;
2. interference with normal functions of guard cells;
3. poisoning of plant cells after diffusion of acidic substances through stomata or cuticle;

4. disturbance of normal metabolism or growth processes without necrosis of plant cells;
5. alteration of leaf root-exudation processes;
6. interference with reproduction processes; and
7. synergistic interaction with other environmental stress factors.

Increase in soil acidity also can be detrimental to the chemical availability of several essential nutrients. Over several decades of acidic deposition, one can expect a net loss of cations (Ca^{2+} and Mg^{2+}, both important for plant growth) from low base exchange conditions. Under conditions of low cation availability, any further loss of cations should be considered significant, however small that loss may be. Much of the northern United States and eastern Canadian forest industry is founded on these low-pH and low-nutrient soils.

The increase in soil acidity also can lead to mobilization of other elements (Al, Mn, and Fe), sometimes in quantities toxic to terrestrial plants as well as to aquatic ecosystems. One of the indirect effects of watershed acidification is the mobilization of aluminum in soils, with the potential to cause toxic effects to terrestrial organisms and the biota of streams and lakes (Ulrich *et al.*, 1980). Aluminum solubility is pH-dependent, and increases with increasing acidity. Several reports have documented elevated aluminum concentrations in acid lakes and streams in areas known to be impacted by acid inputs, and in effluents from lysimeters treated with acid solution (Abrahamsen *et al.*, 1976). While aluminum is typically leached from the upper soil horizon of podzol soils by carbonic acid and organic chelation, it is usually deposited in lower horizons.

Much research on aluminum toxicity has been conducted on crops and legume species (Foy *et al.*, 1978). Excess aluminum affects cell division in roots, causing inhibition of root growth, leading to stubby and brittle roots. It generally accumulates in roots and is only found in above-ground plant parts of a few plant species. In addition, excess aluminum fixes phosphorus in less available forms in the soil and in or on plant roots. Consequently, phosphorus deficiency is often associated with toxic aluminum concentrations and is generally the form of symptom expression in above-ground plant parts.

Evaluating soil sensitivity to these processes is important for both terrestrial and aquatic ecosystems. Two systems for classifying soil sensitivity have been suggested, one by McFee (1980) and one in Canada by Coote *et al.* (1980). McFee's approach is based on the cation exchange capacity (CEC) of the

soil. High CEC implies strong buffering capacity, while low CEC soils may experience rapid pH drops as a result of acid deposition or, and if they are already acid, may release aluminum. The fundamental criteria and assumptions for establishing the classification system are as follows:

1. acidic deposition over a 25-yr time span;
2. 100 cm precipitation per year, pH 3.7;
3. 25 cm soil layer, 1.3 gm/cm^3 bulk density;
4. acid additions equal to between 10 and 25 percent of CEC could be significant.

Utilizing large-scale soil maps, McFee (1980) estimated that about half of the soils in the eastern United States are "slightly sensitive" or "sensitive" to acid deposition and summarized the results in a map format. The above assumptions and criteria result in three sensitivity classes:

Non-Sensitive:
Soils with Free Carbonates
Soils Frequently Flooded
CEC > 15.4 meq/100 gm

Slightly Sensitive:
CEC = 6.2 - 15.4 meq/100 gm

Sensitive:
CEC < 6.2 meq/100 gm

Forest site index also can be used as a measure of terrestrial ecosystem stress from acidic deposition and an integrator of effects from nutrient additions (or losses) and the toxicity of aluminum, hydrogen ions, and heavy metals. A large body of literature details the effects of pH and stress on the biotic community; but to date, there has been no integrated study to determine whether reductions in terrestrial biomass productivity could be due to acid precipitation. Estimation of the change in forest site index over 20 yr or more is one approach to consider (Loucks *et al.*, 1981). To determine site index for a forest, one uses the height and the age of the dominant and co-dominant trees (Curtis *et al.*, 1974). Plotting height versus age (Figure 3) of each stand results in a series of points which can be broken down into several arrays, over age, each array representing a separate site class. The site index takes the form of the "height at a given time" (i.e., a site index of 80 is a height of 80 ft at 45 yr).

On forest lands where no trees are present, soil properties have been used in multiple regression models to predict site

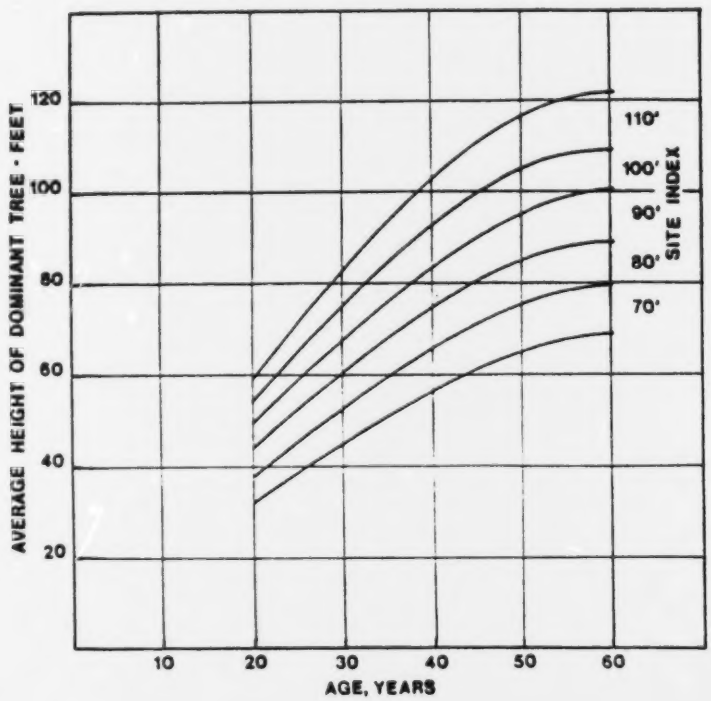

Figure 3. Site index classes determined by plotting age against the average height of dominant trees. Cation depletion by acid rain could reduce the position of some portions of the curves.

index. Fralish and Loucks (1975) developed such a model for trembling aspen in Wisconsin using the content of nutrient cations such as calcium and magnesium, which can be stripped by acid additions. The hypothesis that needs to be explored here is that depletion of this cation pool over 2 to 3 decades could alter the site index response, as estimated by the regression relationship, so that height growth, and, therefore, annual forest biomass production, was reduced significantly.

Thus, use of the site index as an integrator of acid deposition effects (via nutrient stripping and aluminum toxicity) has the advantage of being readily convertible to economic terms for cost-benefit analysis. At this time,

however, we continue to lack sufficient support to test the hypothesis, even with existing data.

POTENTIAL ALTERATION OF SURFACE AND GROUNDWATER

The addition of acidic pollutants to a lake/watershed ecosystem is coming to be thought of as a large-scale quasi-titration (Henriksen, 1980), but it is a complex, uneven process, only superficially similar to a laboratory titration. Gorham and McFee (1980) and Last et al. (1980) discuss the variables involved and note that the hydrogen ions deposited with precipitation (or generated by other components of precipitation) may have four fates in the lake-watershed system:

1. where carbonates are present, hydrogen ions will be consumed, with the release of bicarbonate and calcium or magnesium;
2. hydrogen ions may be exchanged for various metal cations in soils with appreciable cation exchange capacity (McFee et al., 1976);
3. hydrogen ions may react with alumino-silicates or other minerals, releasing metal cations; and
4. any hydrogen ions not neutralized by the above processes will enter aquatic ecosystems in association with a mobile anion, usually sulfate.

The first three processes above account for the observation that surface waters are less acid than the precipitation they receive (Wright and Henriksen, 1978). However, other considerations include the mobility of anions such as sulfate, and the breakdown of ammonium ions to yield acidity. Alteration of groundwater and small-stream flows appears to represent a combination of factors.

Researchers differ and the evidence is somewhat conflicting as to whether the geochemical alteration of watersheds due to acidic inputs should be viewed as irreversible and, if so, on what scale. Irreversibility can be viewed as a failure to recover over geological time, but for natural resource systems, an incomplete recovery to a prestressed or undamaged state over a few decades, for all practical purposes, may be regarded as irreversible.

The possibility of irreversible loss of buffering capacity in lakes and watersheds is one of the most serious potential impacts of acid deposition. The ability of lake water to resist pH depression when acid is added (i.e., buffering capacity) depends on its alkalinity. The alkalinity of the water depends

on the presence of anions or other species which can take up protons. In most natural waters, alkalinity is largely a function of bicarbonate, but other substances such as organic acids, silicates, and ammonia are important in the low alkalinity lakes most susceptible to acidification. When lake water is titrated with acid, the change in pH per unit of added acid (i.e., the slope) varies as successive buffers are protonated, each acceptor taking up protons in its own characteristic way.

When titration is considered for an entire watershed, as may be the case from sustained long-term atmospheric acid inputs, the same buffering processes can occur. However, the reaction is much more heterogeneous in a watershed, and the total quantity and variety of proton acceptors are probably greater. Contact between protons in water and the solid buffering materials in the soil is not assured, depending on hydrologic flow patterns within both the upper ("inter-flow") and deeper soil horizons. Periods of peak runoff, when much of the "surface" water penetrates only a few centimeters into the soil, are often associated with acid flushing (low pH), apparently with little buffering. This process is more likely to occur when watershed buffering is naturally low or may have been depleted by long-term acid input.

The hypothesis that acidification of surface waters by atmospheric acid inputs can be viewed as a large-scale titration has been articulated by Henriksen (1980) and supported with data from North America and Scandinavia (Wright et al., 1980). Nearly all lakes, except those dominated by acid bog drainage water, are normally bicarbonate buffered with pH greater than 6.5. By stoichiometry, addition of acid from the atmosphere will consume alkalinity, but the pH will fall only slightly as long as some bicarbonate remains. Long-term (more than 50 yr) records of decreasing alkalinity in a water supply reservoir in the Adirondacks suggest that alkalinity has declined with the continued atmospheric acid input (Schofield, personal communication). As bicarbonate (and any other buffers) are depleted, and sulfate ions can no longer be retained in the soil, Henriksen suggests lakes enter a transition phase characterized by severe pH fluctuations (1 to 2 units) and associated stresses on fish and other aquatic biota. This transition phase is a time when the lake is particularly susceptible to seasonal pulses of acid (e.g., snowmelt) and to the incomplete "mixing" of water and soil during flushing events. According to this view, a lake may exist in a transition phase until it is sulfate-saturated and the last carbonate or other buffering above pH 5.6 in the watershed is consumed.

ARE WATERS OF THE WESTERN GREAT LAKES ENTERING A "TRANSITION"?

The hypothesis of a relatively irreversible titration of the geochemical components contributing buffering capacity is a simplification of the complexities of lake/watershed processes. The variety of potential sources of buffering, water flow patterns, and rates of acid deposition and flushing all tend to make each lake/watershed system unique. However, the general pattern of observed responses is consistent with the known sulfate saturation and low buffering capacity of the geology and soils in the affected areas, and these conditions do extend through Wisconsin and Minnesota.

At the present time there is no single, fully validated methodology for projecting the alteration of aquatic systems from acid deposition. Thus, measures of aquatic sensitivity to acid inputs should be thought of as hypotheses constructed with a reasonable amount of quantitative inputs, but evaluation should not be based on any one model or measurement procedure. The three methodologies given below are limited in scope and/or availability of data, but taken together they present a comprehensive view of our ability to quantify current resource status and, therefore, make some prediction of the potential for future change in the western Great Lakes area.

The Calcite Saturation Index (CSI)

Kramer (1976) has summarized the relationship between pH and alkalinity in the calcite saturation index (CSI), which expresses the relative saturation of water with calcium carbonate:

$$CSI = p(Ca^{2+}) + p(Alk) - p(H^{+}) + pK$$

where $p(X) = -\log_{10}X$, $pK = 2$, (Ca^{2+}) is given as mol/l, and (Alk) and (H^{+}) are given as equivalents/l. When $CSI < 1$, the lake is nearly saturated with calcium carbonate and not susceptible to acidification. Increasing CSI indicates increasing susceptibility, and, at $CSI > 4$, the lake is very likely to be affected by acid (Glass and Loucks, 1980).

The CSI has been used to classify lakes sensitive to acidification (Glass and Loucks, 1980, and others) and is a relatively simple way to account for lake buffering capacity. However, it is not comprehensive enough to be used as a sensitivity index as defined earlier for watersheds because buffering capacity is only one aspect of lake/watershed

sensitivity. Moreover, the CSI reflects only present conditions and does not relate past or future changes to loading rates. There is no indication in CSI of how a lake came to have a particular value, or of any explicit relationship between the CSI and acidic inputs.

The Dickson Relation

Another way to summarize the relationship between lake pH and atmospheric loading of acidic pollutants is to plot lake pH in relation to measured local sulfate loadings, Figure 4 (Almer et al., 1978). Various combinations of watershed characteristics are reflected in the family of curves connecting

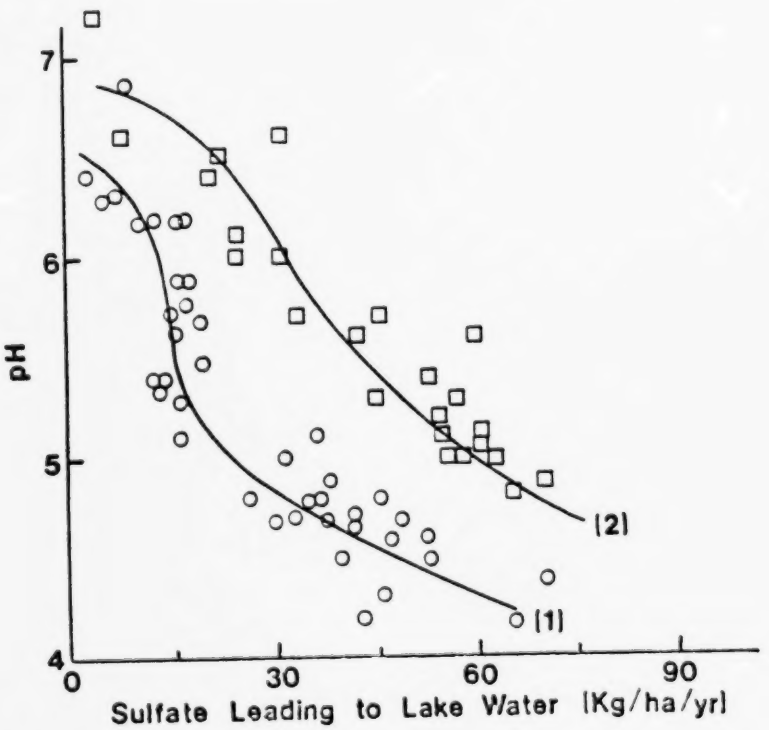

Figure 4. Effects of various sulfate loading rates on lake pH for lakes in very sensitive (1) and somewhat less sensitive (2) surroundings in Sweden. (From Glass and Loucks, 1980.)

the different sets of lake data. A larger number of curves may be envisioned, each representing lake/watershed systems of comparable sensitivities as they apparently respond to increases in atmospheric acid inputs. The curves are superficially similar to titration curves, as might be expected, and each shows buffering at high pH, then a rapid drop (as this buffering apparently is depleted) to lakes with somewhat lower pH and minimal buffering. The pH in the more sensitive lakes drops sooner and more rapidly, relative to the sulfate ion loading.

A graph of sulfate deposition versus lake pH could be used to express lake/watershed sensitivity, and, therefore, acid loading tolerance, by evaluating the position of the lake/watershed system on the response curves. From a knowledge of the response of very sensitive geochemical/biological systems in moderately impacted systems, it appears possible to anticipate similar responses in the future on similarly sensitive systems if acidic inputs increase or are sustained.

Examination of Figure 4 suggests that annual sulfate loadings of less than 15 to 17 kg/ha would be unlikely to degrade lakes of the type represented in curve (1). However, if the lower envelope of the data distribution is viewed as a potential "family" of the most sensitive lakes and streams, these appear to be just barely free of potential acid loadings effects at an annual rate of 9 to 12 kg/ha/yr. Thus, two "tolerances" can be defined, one associated with a possible protection of nearly all sensitive aquatic resources, and the other with protection of something less than all sensitive lakes; e.g., only the half of the "sensitive" resources that lies above curve (1) in Figure 4.

The Henriksen Nomograph

Henriksen (1980) presents a model based on the concepts implicit in titration of a bicarbonate-buffered lake with strong acid (principally sulfuric acid) from the atmosphere. In the process, bicarbonate is depleted and lake pH can fall below 5 with consequent effects on aluminum mobilization and fish. These relations are basically the same as those in the Dickson work, and are summarized in the nomograph (Figure 5) using two key measurements:

1. ambient concentrations of in-lake calcium (or Ca plus Mg) as an estimator of the pre-acidification alkalinity; and

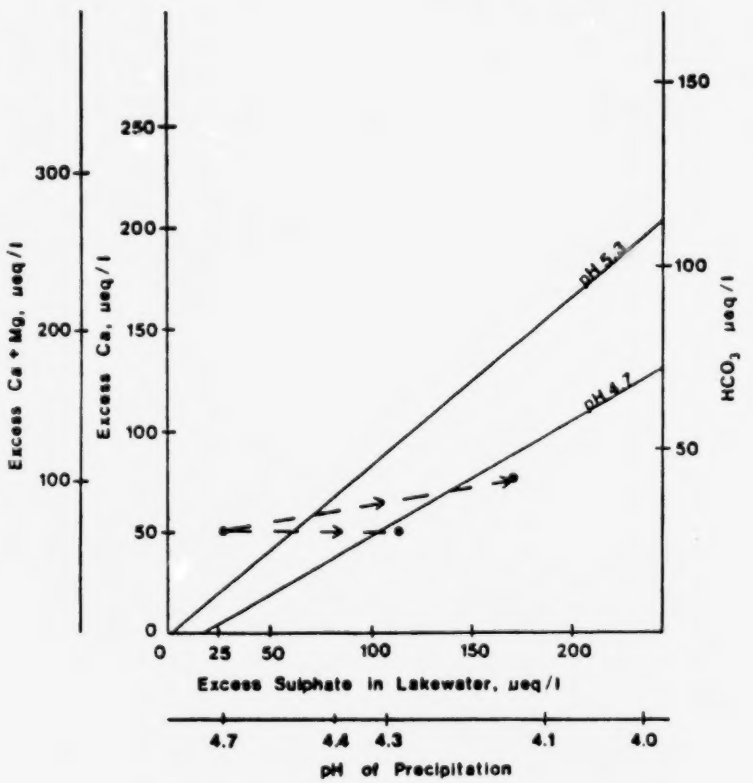

Figure 5. A nomograph to predict the pH of lakes given the sum of non-marine calcium and magnesium concentrations (or non-marine calcium concentration alone) and the non-marine sulfate concentration in lake water (or the weighted-average hydrogen ion concentration in precipitation). Nomograph also can be used to predict future changes in lake pH when precipitation acidity increases (from Henriksen, 1980).

2. lake sulfate concentrations (in excess of marine input) as an estimator of H^+ added to the system.

The resulting semi-predictive nomograph is divided into three sections:

1. bicarbonate lakes, where original alkalinity was high and/or added H^+ is low, so that the lakes remain bicarbonate-buffered;
2. acid lakes, where original alkalinity was low relative to acid inputs, and all bicarbonate appears to have been depleted by the acid addition; and
3. transition lakes, in which bicarbonate appears to be undergoing reduction (or is almost depleted) and large pH fluctuations occur during runoff events.

The transition phase, in which the lake is shifting from a bicarbonate-buffered equilibrium at moderate pH to an aluminum-buffered equilibrium at low pH, represents the key process requiring prediction. This shift apparently is forced by H^+ and sulfate ion inputs, and Henriksen presents regression equations based on Norwegian lake and precipitation data for representing sulfate in lake water(SO_4^*) in terms of sulfate in precipitation [$SO_4(p)$] and H^+ in precipitation [$H^+(p)$] :

$$SO_4^* = -19 + 1.9\ SO_4(p)$$

$$SO_4(p) = -2.7 + 1.37\ H^+(p)$$

All concentrations are in microequivalents per liter (ueq/l), and the sulfate is excess over that from marine origin. These equations have not yet been validated for North America.

CONCLUSIONS

Ultimately, even the acidification of surface water resources is of little consequence unless the productivity of resources is altered in ways that are important to human welfare. Many of the chapters which follow will address what we know and do not know about these questions. Let me turn here only to the question of the processes by which a regional experi-mental manipulation appears to be underway in the Great Lakes states: perhaps 50 yr of relatively high levels of acid additions in the eastern areas, and as little as 20 yr of moderate to low levels of acidic deposition in the western areas. Research must answer whether the duration of treatment is equivalent to intensity of treatment. How many years do we

have before "significant" (yet to be defined) effects may be expressed in the lightly impacted regions?

The geography and resources of the Great Lakes region make very plain the great importance of these questions, for some states more than others. Decisions regarding industrial development in this region are being made every day, and investments in large industrial plants are relatively irreversible, at least within a generation or two. So too, apparently, are some of the effects of acid rain. The approaches that scientists and government leaders in the Great Lakes region take in evaluating these issues are likely to have considerable impact on others in the United States and Canada.

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